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USSR WORK ON BIOCHEMICAL CONCENTRATION OF ELEMENTS

[Comment: This is a translation of an article by Yu. A. Zhdanov entitled "Concerning the Utilization of the Capacity for Biochemical Concentration of Elements" which was published in Priroda, Vol 44, No 6, June 1955, pp 89-93. The author of this article not only points out that the capacity of plants of some botanical species to concentrate selectively certain elements can be used in prospecting for useful minerals (e.g., zinc and iron ores): he also advocates utilizing this property of living matter (particularly as far as bacteria, algae, and fungi are concerned) in the industrial concentration of rare elements after suitable varieties which are sufficiently productive as bioconcentrators have been developed for this purpose. To convince the readers that this method is feasible, he cites a number of instances of the application of living organisms in the processing of large volumes of liquid, giving as one of the examples the removal of radioactive isotopes from industrial wastes. In connection with prospecting for ores, the fact that Asperigillus niger may utilize uranium in its metabolic processes when there is a shortage of zinc (see below) seems to be of interest.

Numbers in parentheses refer to the author's bibliography appended.]

Industrial activities involve the concentration and use of a great number of chemical elements. At present, practically all the known elements comprising the periodic system are utilized industrially. As a result of the increased demand for raw material, the depletion of rich deposits, and improvements in the methods of extraction, practical use is made of an increasing number of poor sources of useful minerals and of an increased number of minerals and elements which occur in a dispersed state.

During the past century, the content of useful metals in industrially exploited ores has dropped considerably. For instance, at the beginning of the 19th century copper ores containing about 10% of copper were exploited. In the period 1881-1890, the average content of copper in US copper ores comprised 5.2%; in 1891-1900, 3.8%; in 1901-1910, 2.06%; in 1911-1920, 1.84%; and in 1921-1930, 1.49%. At present this content is close to 1%. The same trend can be observed in regard to many other elements. As a result, there is an increased interest in the utilization of industrial and agricultural wastes and of such types of crude material as sea water and other naturally occurring solutions.

It is known that the concentration of chemical elements in the course of industrial production is only one aspect of the matter. The constantly progressing physical deterioration and chemical decomposition of industrial products brings the substances involved into a state of high dispersion, with the result that the extraction of the elements in question becomes very difficult. Every year, huge quantities of iron, aluminum, copper, and zinc are lost as a result of corrosion or are discarded in the form of industrial wastes. It is estimated that in England about 30% of the total production of steel serves for the replacement of losses due to corrosion.

Many valuable products are constantly wasted with industrial effluents that are released, and only an insignificant portion of these products is recovered. Thus, the effluents of ore concentration plants contain significant quantities of nonferrous metals. At an average expenditure of 5 cubic meters of water for the treatment of 1 ton of ore, 1 liter of effluent contains 0.4-8

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milligrams of copper, up to 1 milligram of zinc, and up to 10 milligrams of lead. One of the plants which produces tin from waste metal releases daily into the effluent waters approximately 4 kilograms of tin, 3.8 kilograms of lead, up to 2 kilograms of copper, and 15-20 kilograms of zinc. Partial recovery of these metals is carried out by precipitation methods and requires considerable expenditures.

Natural solutions, such as sea water and the water of lakes, rivers, and springs represent an inexhaustible source of chemical crude material. The industry uses these waters for the production of a number of chemical substances, i.e., sodium chloride, sodium sulfate, soda, borates, bromides, iodine, etc. However, the bulk of useful elements contained in natural waters is not being used as yet, because their extraction involves large expenditures of energy and of chemical reagents. It is sufficient to recall that 1 ton of sea water contains 380 grams of potassium, 65 grams of bromine, 13.3 grams of strontium, 1.3 grams of fluorine, 200 mg of rubidium, 50 mg of iodine, and 2 mg of cesium. (1)

Even the fresh water of rivers contains a considerable quantity of valuable substances. For instance, the river Don transports every year into the Azov Sea 7,950 tons of fluorine, 4,365 tons of bromine and iodine, 530 tons of boron, and 4.5 tons of arsenic. (2) If it is taken into consideration that the total mass of the hydrosphere comprises 1.40×10^{18} tons, it will become obvious that huge resources of crude material are contained in the natural aqueous solutions.

The treatment of dilute solutions formed by natural waters and by industrial effluents involves great technical difficulties and requires a new approach. One of the possible ways of making this approach, as indicated by nature itself, can be the utilization of the capacity of living organisms to accumulate selectively individual elements in the course of biosynthesis.

The important geochemical function fulfilled by living matter is generally recognized at present. Numerous investigations have shown that the direction and manner of migration of chemical substances, as well as the forms in which many chemical substances are accumulated, are closely connected with the vital activity of animals, plants, and microorganisms. USSR science has led in the discovery and elucidation of relationships pertaining to this natural process.

Academician V. I. Vernadskiy and his pupils have participated to a prominent extent in work in this field. In his Biogeokhimicheskiye Ocherki (Biogeochemical Essays) Vernadskiy formulates his views on this problem in the following manner: "Living matter plays an entirely exceptional role as far as its influence on the natural environment is concerned. It has given rise to all fuels on which our present-day life is based: coal, brown coal, bituminous coal, combustible shales, petroleum, peat, and finally sapropelites in the larger sense of the word represent products of its activity. The vital activities of living beings determine the composition of the atmosphere (they are the main supplies of free oxygen and also of nitrogen), the chemistry of the sea (particularly the composition of sea water), and the character of natural waters (river and lake waters), and of fresh, saline, and some mineral wells. Living beings are responsible for the formation of deposits of limestone and dolomites.

"Processes connected with the occurrence of marine and lake silts and phenomena taking place in the soil of dry land are closely connected with manifestations of life, and living matter comprises several tens of percent of the weight of this matter. The occurrence of iron, manganese, and aluminum ores is connected to a great and possibly to a major extent with manifestations of life. Vital processes are responsible for phosphorite deposits and

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for those of nitrates and elemental sulphur. The formation of some ore deposits, namely those of copper, vanadium, silver, and lead is also apparently connected with vital activities. In the gas exchange occurring on earth, living matter, in addition to regulating the composition of the atmosphere, also plays a decisive role in the formation of hydrogen sulphide, nitrogen, sulphur dioxide, methane, carbon dioxide, oxygen, and water." (3)

Living organisms at various stages of the development of the organic world evince a remarkable capacity for concentrating to a great extent various elements from the environment, particularly from aqueous solutions. Extensive research in this field was conducted by Vinogradov and his collaborators. In the course of the work done by them, important but hitherto little-known correlations between the composition of organisms, their evolution, and Mendeleyev's law of the periodic system of elements were established. (4)

Many instances of a high concentration of individual elements by living organisms are cited in an investigation by Vinogradov entitled "Khimicheskiy Elementarnyy Sostav Organizmov Morya" (The Elemental Chemical Composition of Marine Organisms.) Similar data are reported in other communications by this author. To illustrate, let us give several examples.

Vanadium is one of the disperse elements which is concentrated by some organisms. Its average content in the earth crust comprises 0.015%. At the same time, as the work of Vinogradov has shown, the bodies of Acsidia inhabiting the Kola Bay contain 0.04-0.5% of vanadium, which enters into the composition of the blood corpuscles of these marine animals. Vanadium is also concentrated by some fungi, particularly the red fly agaric.

The high biochemical activity of zinc and its participation in a number of enzymatic and hormonal systems (specifically, zinc is contained in carbonic anhydrase) have resulted in a considerable accumulation of this element in many organisms. The soil contains only 0.005% of zinc. Many soil microorganisms, plants (e.g., the violet), and particularly fungi concentrate zinc to a considerable extent. Thus, 1 kg of the dry matter of puff balls (Lycoperdon giganteum) contains 0.242 grams of zinc. The quantity of zinc concentrated by oysters from sea water comprises 1.5-7.0 grams per kilogram of dry matter.

It is known that germanium has acquired a great significance for modern technology. The most important source of this valuable element is the ash of fossil coal, i.e., a remnant of ancient flora. Research on the subject has shown that while on the average the content of germanium in the earth crust amounts to 7×10^{-4}%, up to 0.001% are accumulated in the ash of leaves and grass. The ash of some coals found in the Don Basin and in the Ural Coal deposits contains up to 0.1-1% of germanium.

The skeletons of representatives of one of the Radiolaria (Acantharia) classes consist predominantly of strontium sulfate. The skeletons of these animals have accumulated strontium and have played a major role in the formation of deposits of celestine. In the liver of the mollusk Pecten maximus, cadmium is accumulated to the extent of 0.05-0.2% (with reference to the dry weight), a figure which exceeds by a factor of tens of thousands the concentration of this element in sea water. (5)

Brown algae of far-eastern seas contain up to 0.5% of iodine when they are in an air-dry state. Gastropodes of the order Alcoynaria concentrate bromine to a considerable degree. Marine plants and animals contain approximately 100 times more radium than the surrounding water; plants of the genus Lemna concentrate radium from the water in amounts which are even 20 to 500 times larger than that. Marine algae concentrate rubidium by a factor amounting to multiples of ten, while fresh water plants concentrate this element from the environment by a factor amounting to thousands. (6)

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Among bacteria there are species which concentrate iron, manganese, aluminum, sulphur, silicon, and calcium. Many more examples can be given. Vernadskiy once wrote: "Organisms that occur in the oceans concentrate in addition to oxygen and hydrogen the following elements in amounts comprising more than 10% of their weight: calcium, iron, magnesium, barium, strontium, and possibly also phosphorus, manganese, and sulphur. These are specific calcium, silicon, iron, magnesium, and other organisms in which the quantity of the element in question may exceed by many tens, hundreds, and thousands of times the normal average content [of the element] in their bodies" (7).

Academician N. M. Strakhov has shown in his investigations that the processes of the formation of deposits taking place in contemporary marine bodies of water involve first of all biogenic extraction of elements and only to a smaller extent purely chemical precipitation. In the course of the evolution of the earth, there has been a relative increase of the role of biogenic precipitation as compared with chemical precipitation.

A number of examples of the utilization of the capacity of organisms to concentrate elements from dilute solutions can be given from contemporary industrial practice.

A considerable quantity of iodine is extracted at present from marine algae, phosphorus is obtained from the bones of animals, and potassium from the ash of plants. The production of potassium from the ash of algae is being expanded, in view of the fact that the content of potassium salts in this ash reaches 35%. Calculations have shown that if brown algae of the genus Macrocystis are used, one may obtain up to 2,200,000 tons of potassium chloride per year from an area amounting to about 100,000 hectares. (8)

Biological methods are also being applied in the purification of waters from harmful radioactive impurities. For example, the removal from industrial effluents of radioactive phosphorus P^{32} and of radioactive I^{131} can be carried out with the aid of the microflora of active silt. N. G. Kholodnyy in his monograph Zhelezobakterii (Iron Bacteria) states that in a certain German city, for the purpose of eliminating manganese from the water supply, the water was passed through sand filters which had been inoculated with cultures of iron bacteria. It was found that the bacteria assimilated all of the manganese from the water.

The capacity of plants to concentrate certain elements has been used in recent times to an increased extent in prospecting for ore deposits. Vinogradov states that there are increased concentrations of nickel, chromium, cobalt, copper, zinc, and molybdenum in the ash of plants collected from soils located above the corresponding ore deposits. Over zinc deposits special "calamine" plant life appears which concentrates zinc. Among these plants are the violet, mokritsa vesennyaya [Arenara verna?] and others. The application of the botanical method in prospecting for iron ores has been described; the region under investigation is mapped according to the content of iron in the leaves of plants and zones of an increased concentration of the metal in the soil are established on this basis.

Observations carried out on the properties of living organisms and the utilization of these organisms in a number of cases by reason of their capacity to concentrate elements enable us at present to approach this problem from a broader standpoint and in a more effective manner. The practical problem of concentrating elements by biosynthetic methods on an industrial scale requires the solution of a number of scientific and technical problems which do not present insurmountable difficulties.

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The level which has been reached at present by agricultural science and technical microbiology furnishes the necessary prerequisites for expanding the work on the selection of plants from which highly productive strains capable of concentrating chemical elements will be bred. First of all, one ought to concentrate on increasing the productivity of organisms which accumulate certain elements under natural conditions. Especially suitable for this purpose would be bacteria, algae, and fungi. The work which is being carried out by microbiologists on the selection of microorganisms that produce antibiotics and fermentation products (e.g., alcohols, organic acids, sugars, acetone, etc.) indicate in which manner the problem under consideration can be solved. One cannot leave out of consideration the fact that the initial strain of the fungus which is used for the production of penicillin by the method of submerged growths had an activity amounting to only 40-80 units per milliliter. As a result of selection work on cultures subjected to irradiation with X rays and ultraviolet rays, the productivity of the initial strain could be raised to 1,000 units per milliliter and more.

Using the principles of michurnist biology, one may aspire to solve also the second, more complex problem: namely, that of the creation of forms of organisms which will concentrate some specific, predetermined element. Possible ways of achieving a solution of this problem are indicated by the capacity of iron bacteria, which has been noted above, to concentrate in the absence of iron the manganese from the surrounding medium.

The fungus Aspergillus niger uses uranium for its metabolic reactions when there is a shortage of zinc. As a result, the content of uranium in this fungus may increase by a factor amounting to multiples of 10 as compared with the environment. Selenium, which is similar to sulfur in its chemical behavior, may to a certain extent replace the latter in such physiologically important compounds as cystine, cysteine, and methionine. The element selenium has become indispensable to some plants of the genus Astragalus which grow on soil that is rich in selenium. This element accumulates in the plants in question in quantities reaching 1.25 grams per kilogram of weight, which is a concentration hundreds of thousands of times higher than that usually found in the soil. At this stage, nothing definite can be said as yet about the significance of the concentration of niobium in organisms and the physiological role played by this element. However, experiments in which radioactive niobium Nb^{95} was introduced into the soil demonstrate that this element is being absorbed by plants in an intensive manner.

Facts of this order give rise to the hope that work on the development of organisms which will accumulate a definite chemical element will prove successful.

It is obvious that only the concentration of elements which seldom form ore deposits or are invariably found in a dispersed and diffused state will prove of practical interest. There is no point in accumulating artificially by the biological method such elements as calcium, chlorine, iron, silicon, and sodium, because rich and accessible deposits of these elements are available in nature.

Application of methods of biochemical concentration to commonly occurring elements of which there is no shortage would be practically feasible only for such purposes as the biological purification of water or prospecting for useful minerals. In the latter case, one might consider the possibility of breeding special indicator organisms similar to those which are available at present for vitamins, amino acids, etc. The examples cited of the accumulation by organisms of such dispersed, rarely occurring, and unusual elements as iodine, bromine, selenium, germanium, cadmium, rubidium, niobium, vanadium, etc., make it possible to assume that biochemical concentration will serve a definite practical purpose as far as these elements are concerned.

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It does not appear too improbable that organisms which accumulate in their skeletons the salts of calcium and magnesium could yield initial strains for the breeding of organisms that will be useful in the biological concentration of strontium or lithium.

The contemporary technical biochemistry and microbiology and the existing methods of treatment of water supplies and aqueous effluents furnish the necessary technological prerequisites for the breeding of living concentrators of chemical elements under production conditions.

Microbiologists and chemists have developed methods of surface and submerged culturing of microorganisms, of feeding and protecting these microorganisms, and also of extracting products of their metabolism. The water treatment stations of large cities treat hundreds of thousands of cubic meters of water per day and the same amounts of effluent waters originating at cities and industrial enterprises are subjected to purification from chemical and other admixtures. The available methods of filtration, aeration, precipitation, and fermentation of large volumes of liquid can be used for the purposes suggested in the present article. It has already been emphasized by Vernadskiy that as far as the rapidity of concentration of solid substances from their dispersed state is concerned, the biogeochemical energy is probably the greatest available effective force that exists on earth, if the process in question is considered within the scope of geological time. The action exerted by this force can and should be utilized in a planned and directed manner for the purpose of concentrating substances at a rapid rate for industrial purposes.

Taking into consideration the huge resources of raw material available in sea water, the high rate of propagation of algae, and the experience which is available as far as the utilization of algae is concerned (including artificial planting in China and Japan), one must conclude that it would be advisable to do work on the selection of algae on an extensive scale. On being protected under production conditions from their natural enemies, the organisms capable of acting as bioconcentrators will function very effectively. If appropriate living organisms have been developed, the extraction of dispersed elements by biochemical method from large volumes of dilute aqueous solutions will become entirely feasible.

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